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Mass Spectrometric Studies at High Temperatures. XII. Stabilities of

Dysprosium, Holmium, and Erbium Subfluorides

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The high-temperature equilibria among the vapor species produced by the reaction of Ho metal with HoF₃, DyF₃, and ErF₃ were studied with a mass spectrometer. The sub-fluorides of all three metals were identified and their ionization potentials were measured. From the temperature dependence of the equilibrium constants, one can calculate heats of reaction, the dissociation energies of the monofluorides, and the heats of atomization of the diffuorides and trifluorides.

I. Introduction

The mass spectrometric high-temperature study of the $Nd-NdF_3$ system¹ showed the possibility of using the reaction among the rare earth metals and fluorides as a means for producing the subfluorides and determining their dissociation energies. In the work reported here, a mass spectrometric study was made of equilibria involving the atoms and subfluorides of Dy, Ho, and Er.

II. Experimental Section

The apparatus and experimental procedure were described in the previous papers of this series.¹ The chemicals were purchased from Semi-Elements, Inc., Saxonburg, Pa., and were used without further purification.

III. Results

The subfluorides of Dy, Ho, and Er were produced by heating a mixture of DyF_3 and ErF_3 with Ho metal in the Ta Knudsen cell. In a separate experiment, HoF₃ was heated with Ho metal. The ions M⁺, MF⁺, and MF₂⁺ of all three metals were identified in the vapor above the mixture. In Table I are listed the appearance potentials and the neutral precursors of various ions. The appearance potential of the DyF_2^+ ion was not measured due to the interference of a large background mercury peak.

The appearance potential measurements indicate the presence of M, MF, MF₂, and MF₃ species in the effusing vapor. The appearance potentials of Dy^+ , Ho⁺, and Er^+ ions are close to the ionization potentials of the elements measured by a surface ionization method.^{2,3} It is interesting to note the low values of the ionization potentials of the mono- and diffuorides of the rare earths.

The heats of the various reactions were determined

⁽¹⁾ K. F. Zmbov and J. L. Margrave, to be published.

⁽²⁾ N. I. Ionov and M. A. Mitsev, Zh. Ekspim. Teor. Fiz., 38, 1350 (1960).

⁽³⁾ N. I. Alekseev and D. L. Kaminskii, Zh. Tekhn. Fiz., 34, 1521 (1964).



Figure 1. Second-law plot of the mass spectral data for the heterogeneous reaction $3HoF(g) = 2Ho(g) + HoF_{a}(s)$.

Table I: Appearance Potentials and Neutral Precursors ofthe Ions over $DyF_{3} + ErF_{3} + Ho$ Mixture

Ion	A.P., ev	Neutral
Dy+	5.8 ± 0.1	$\mathbf{D}\mathbf{y}$
Ho+	5.9 ± 0.1	Ho
\mathbf{Er}^+	6.1 ± 0.1	\mathbf{Er}
DyF+	6.0 ± 0.3	\mathbf{DyF}
HoF+	6.2 ± 0.3	HoF
ErF +	6.3 ± 0.3	\mathbf{ErF}
HoF_2^+	7.0 ± 0.3	HoF_2
	12.5 ± 0.5	HoF3
ErF ₂ ⁺	7.0 ± 0.3	\mathbf{ErF}_2
	12.5 ± 0.5	ErF₃

from the measurements of the temperature dependence of the ion currents at electron energies 5 ev above the thresholds, and applying appropriate corrections for dissociative ionization. Plots of the ion-current analogs of the equilibrium constants (k_i) vs. 1/T are shown in Figures 1, 2, and 3.

Table II lists the heats for reactions as obtained by the second-law treatment of the data. ΔH°_{298} of the reactions 1-4 were calculated by using the literature data⁴ for the heat capacity of Ho(g), and estimated values for HoF(g), HoF₂(g), and HoF₃(g). The heats of the exchange reactions 5, 6, and 7, which represent



Figure 2. Second-law plots of the data for equilibria involving the subfluorides of holmium.



Figure 3. Second-law plots of data for exchange reactions between the subfluorides of Ho, Dy, and Er.

(4) K. K. Kelley, U. S. Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.

	Av T ,		ΔH° T,	ΔH°_{298} ,
No.	°K	Reaction	kcal mole ⁻¹	kcal mole-1
(1)	1369	$3HoF(g) = 2Ho(g) + HoF_3(s)$	-127.6 ± 2.0	-141.8 ± 5.0
(2)	1369	$3 \operatorname{HoF}(\mathbf{g}) = 2 \operatorname{Ho}(\mathbf{g}) + \operatorname{HoF}_{3}(\mathbf{g})$	-21.0 ± 4.1	-31.2 ± 6.0
(3)	1369	$3 \operatorname{HoF}_2(\mathbf{g}) = 2 \operatorname{HoF}_3(\mathbf{g}) + \operatorname{Ho}(\mathbf{g})$	17.0 ± 2.3	22.0 ± 5.7
(4)	1369	$HoF_2(g) + Ho(g) = 2HoF(g)$	3.1 ± 2.3	4.5 ± 2.3
(5)	1446	Ho(g) + DyF(g) = HoF(g) + Dy(g)	-2.7 ± 1.2	-2.7 ± 1.2
(6)	1446	HoF(g) + Er(g) = Ho(g) + ErF(g)	-6.0 ± 1.0	-6.0 ± 1.0
(7)	1446	$HoF_2(g) + Er(g) = Ho(g) + ErF_2(g)$	-4.6 ± 1.4	-4.6 ± 1.4
(8)	1446	$HoF_3(g) + Er(g) = Ho(g) + ErF_3(g)$	-5.2 ± 1.6	-5.2 ± 1.6

Tahla II ·	Heats of	Reactions -	in the	HoF.	Ho-Dy-F	and Ho-Er-F	' Systems
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Table III: Bond Dissociation Energies for Rare Earth Fluorides

	Nd	Dy	Но	Er
D(F2M-F), kcal mole ⁻¹	165 ± 10	(151)	151 ± 10	152 ± 11
D(FM-F), kcal mole ⁻¹	142.5 ± 4.2	(135)	136 ± 6	134 ± 8
D(M–F), kcal mole ⁻¹	130.3 ± 3.0	126 ± 4	123 ± 3	136 ± 4

Table IV: Heats of Formation of Rare Earth Fluorides (kcal mole ⁻

			·····		
Nd	Dy	Ho	Er		
-399 ± 10	-407 ± 15	-405.8 ± 0.6^{5}	-402 ± 10		
-303 ± 10	-290 ± 15	-289.6 ± 3.4	-283 ± 10		
-159 ± 10	-157 ± 10	-157 ± 10	-150 ± 10		
-36 ± 5	-36 ± 10	-40 ± 5	-35 ± 5		
	Nd -399 ± 10 -303 ± 10 -159 ± 10 -36 ± 5	Nd Dy -399 ± 10 -407 ± 15 -303 ± 10 -290 ± 15 -159 ± 10 -157 ± 10 -36 ± 5 -36 ± 10	Nd Dy Ho -399 ± 10 -407 ± 15 -405.8 ± 0.6^{5} -303 ± 10 -290 ± 15 -289.6 ± 3.4 -159 ± 10 -157 ± 10 -157 ± 10 -36 ± 5 -36 ± 10 -40 ± 5		

the differences in dissociation energies of the pair of fluorides, are assumed to represent the differences at room temperature and, therefore, no corrections were made for them.

The dissociation energy of HoF(g) was obtained from reactions 1 and 2 by combining the equilibrium data with $\Delta H_f[\text{HoF}_3(\text{s})]^5 = -405.8 \pm 0.4$ kcal mole⁻¹, $\Delta H_{\text{sub}}[\text{Ho}]^6 = 70.6$ kcal mole⁻¹, $\Delta H_{\text{sub}}[\text{HoF}_3(\text{s})]^7 =$ 116.2 ± 3 kcal mole⁻¹, and $D^\circ_{298}(\text{F}_2)^8 = 37.7 \pm 0.3$ kcal mole⁻¹. From the heterogeneous reaction 1, one calculates $D^\circ_{298}(\text{HoF}) = 130.8 \pm 3.0$ kcal mole⁻¹ and from the homogeneous reaction, D°_{298} (HoF) = 128.4 ± 3.0 kcal mole⁻¹. The mean value for the dissociation energy of holmium monofluoride is $D^\circ_{298}(\text{HoF}) =$ 129.6 ± 3 kcal mole⁻¹ (5.62 \pm 0.13 ev) and $\Delta H_f^\circ_{298^-}$ [HoF(g)] = -40 ± 4 kcal mole⁻¹.

With the known value of $D^{\circ}_{298}(\text{HoF})$ and the experimentally determined heat of reaction 4, one obtains the heat of atomization of holmium diffuoride, ΔH_{at} -

 $[\text{HoF}_2(\mathbf{g})] = 263.7 \pm 7.3 \text{ kcal mole}^{-1}$. An independent estimate of this parameter was made from the heat of reaction 3 and using the data for $\Delta H_f[\text{HoF}_3(\mathbf{s})]$, $\Delta H_{\text{sub}}(\text{Ho})$, $\Delta H_{\text{sub}}(\text{HoF}_3)$, and $D(\text{F}_2)$. This procedure yielded $\Delta H_{\text{atom}}[\text{HoF}_2(\mathbf{g})] = 267.1 \pm 8.0 \text{ kcal mole}^{-1}$ establishing as the mean value $\Delta H_{\text{atom}}[\text{HoF}_2(\mathbf{g})] = 265.4 \pm 8.0 \text{ kcal mole}^{-1}$.

The experimentally determined values of the dissociation energies of holmium subfluorides were then

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⁽⁶⁾ C. E. Haberman and A. H. Daane, J. Chem. Phys., 41, 2818 (1964).

 $^{(7)\,}$ K. F. Zmbov, G. Besenbruch, T. V. Charlu, and J. L. Margrave, to be published.

⁽⁸⁾ D. R. Stull, Ed., "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., Aug 1965, No. PB-168-370, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va.

used to establish the corresponding energies of dysprosium and erbium subfluorides.

The heat of the exchange reactions in (5) and the dissociation energy of HoF yielded $D^{\circ}_{298}(\text{DyF}) = 126.1 \pm 4.2 \text{ kcal mole}^{-1}$. No measurements were made of the $\Delta H_{\text{atom}}[\text{DyF}_2(\mathbf{g})]$ because of the interference of background mercury in the mass spectrum.

From the heats of the exchange reactions 6, 7, and 8 and the dissociation energies of HoF and HoF₂, one obtains the corresponding values for ErF, ErF_2 , and

ErF₃: $D^{\circ}_{298}(\text{ErF}) = 135.6 \pm 4.0 \text{ kcal mole}^{-1}$, ΔH_{at} [ErF₂(g)] = 270.0 \pm 9.4 kcal mole $^{-1}$, and ΔH_{at} [ErF₃(g)] = 421.5 \pm 11.4 kcal mole $^{-1}$.

From these data one can derive the bond dissociation energies summarized in Table III and the standard heats of formation presented in Table IV.

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Effect of Density on the Radiolysis of Propylene¹

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The radiolysis of propylene has been studied at various temperatures both below and above the critical temperature as a function of density. The yields of both H₂ and CH₄ decreased with increasing density at all temperatures. The most striking feature of the data is the apparent constancy of the yield of H₂ and CH₄ in the two-phase region. There also appears to be a density-independent region above the critical temperature. Propylene was irradiated in the presence of O₂ and the results show that in the gas phase the yields of H₂ and CH₄ were sharply decreased. In the two-phase region the inhibitory effect of O₂ is markedly decreased for both H₂ and CH₄. Mixtures of propylene and propylene-d₆, at various densities, were irradiated in the presence and absence of scavenger. Higher molecular weight products were also measured as a function of density, and like H₂ and CH₄ were also found to decrease with increasing density in the density range 0.01 to 0.07 g/cc.

Introduction

Recent studies on the radiolysis^{2,3} and photolysis⁴⁻⁶ of propylene have been concerned with specific information on the individual yields of radicals and their identity and with the nature and importance of ionmolecule reactions. In all cases, the irradiation has been conducted with propylene in a single phase.

There are many reasons in principle to suppose that differences in phase might produce differences in yield or distribution of products, but the existing data are limited^{7,8} and do not permit any firm conclusions to be drawn. This work will attempt to determine the effect of phase on the nature and yield of product formation during the radiolysis of propylene.

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